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ELECTRONIC ABSORPTION SPECTRA OF INORGANIC AND ORGANIC COMPOUNDS OF NITROGEN. II. BUTYL AND AMYL NITRITES

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ELECTRONIC ABSORPTION SPECTRA OF INORGANIC AND ORGANIC COMPOUNDS OF NITROGEN. II. BUTYL AND AMYL NITRITES[1]

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(1) Presented in part at the Air Pollution Symposium of the ~~125th~~ Meeting of the American Chemical Society, New York, New York, September 1957.

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ABSTRACT

The ultraviolet absorption spectra of n-butyl nitrite, t-butyl nitrite, n-amyl nitrite, and i-amyl nitrite in the 2100 to 4000 A. region have been determined in the gas state and in the following solvents: cyclohexane, isooctane, carbon tetrachloride, chlorobenzene, diethyl ether, di-i-propyl ether, p-dioxane, ethyl acetate, acetone, a number of alcohols, and water. The peak positions for n-alkyl and i-alkyl nitrites in the 3000-4000 A. band systems are almost completely independent of solvent. The peak positions for t-alkyl nitrites appear to show a blue shift with increasing dielectric constant of the solvent. The usual solvent effects are complicated by a possible shift in the trans-cis ratio in n-alkyl and i-alkyl nitrites. The short wavelength maxima between 2050 and 2250 A. show a blue shift with increasing dielectric constant of the solvent, which may be associated with an allowed n --> π type electronic transition.

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Although the ultraviolet absorption spectra of alkyl nitrites have been of concern in a number of investigations[2-13], problems remain

(2) W. Kuhn and H. Lehmann, Z. Elektrochem., 37, 549, 552 (1931); Z. physik. chem., B18, 32-48 (1932).
(3) W. Kuhn and H. Biller, Z. physik chem., B29, 1-41 (1935).
(4) H. Elkins and W. Kuhn, J. Amer. Chem. Soc., 57, 296-99 (1935).
(5) H. W. Thompson and C. Purkis, Trans. Faraday Soc., 32, 674-80 (1936).
(6) C. Purkis and H. W. Thompson, Trans. Faraday Soc., 32, 1466-74 (1936).
(7) H. W. Thompson and F. Dainton, Trans. Faraday Soc., 33, 1546-55 (1937).
(8) P. Tarte, J. Chem. Phys., 20, 1570-75 (1952).
(9) R. N. Hazeldine, J. Chem. Soc., 1953, 2525-27.
(10) R. N. Hazeldine and J. Jander, J. Chem. Soc., 1954, 691-5.
(11) R. N. Hazeldine and B. J. H. Mattinson, Ibid., 1955, 4172-85..
(12) H. E. Ungnade and R. A. Smiley, J. Org. Chem., 21, 993-6 (1956).
(13) D. H. Szulezewski, M. Yunker and T. Higuchi, J. Am. Pharm. Assocn., 45, 776-9 (1956).

in regard to solvent effects on peak positions and intensities in the 3000-4000 A. region for this class of compounds. Furthermore, information on the low wavelength peaks in alkyl nitrites is meager. The actual identification of the high and low wavelength band systems with types of electronic transitions appears to be unavailable in the literature. Organic nitrites also are of interest as trace components in some urban atmospheres. Consequently, the ultraviolet absorption spectra of n-butyl nitrite, t-butyl nitrite, n-amyl nitrite, and i-amyl nitrite in cyclohexane, isooctane, carbon tetrachloride, chlorobenzene, diethyl ether, di-i-propyl ether, p-dioxane, ethyl acetate, acetone, a number of corresponding alcohols, and water have been measured. The gas spectra for n-amyl nitrite and i-amyl nitrite were also obtained.

EXPERIMENTAL DETAILS

The alkyl nitrites used included n-butyl nitrite, t-butyl nitrite, n-amyl nitrite, and i-amyl nitrite obtained from K and K Laboratories and Eastman Kodak. These nitrites were subjected to atmospheric and

vacuum distillations during various stages of the investigation. A number of the lots of alkyl nitrites used were dried over calcium chloride.

The stock solutions of alkyl nitrites in the solvents were prepared on a weight basis. These solutions were diluted to the appropriate concentration depending on the intensity of the absorption peak. The spectra in the 3000-4000 A. region were determined using solutions containing about 0.2 percent by weight of alkyl nitrites. The more intense bands at 2050-2250 A. were determined with 0.01 to 0.02 percent solutions.

The solvents used for the ultraviolet determinations on the alkyl nitrites were of spectroscopic purity or reagent grade. The diethyl ether, di-i-propyl ether, and dioxane were further purified by passage through alumina columns to remove peroxides and some residual aldehyde.[14]

(14) W. Dasler, and C. D. Bauer, Ind. Eng. Chem., Anal. Ed., 18, 52 (1946).

The products were tested for peroxides by the potassium iodide method.[15]

(15) J. Rosin, Reagent Chemicals and Standards, D. Van Nostrand Co., Inc., New York, New York, 1955, p. 179.

They were then passed through a column of Molecular Sieve, types 4A and 5A, to remove water and perhaps some alcoholic impurities.

The short wavelength peaks were determined using spectroscopic grade isooctane, cyclohexane, diethyl ether, methanol, isopropanol and distilled water. The measurements were made using both 10 mm. and 1 mm. quartz absorption cells.

The gas spectra were obtained using a one-meter gas cell in a

dynamic system. The alkyl nitrites in an air stream were passed through the cell at about one liter per minute from a diffusion cell apparatus.[16]

(16) M. McKelvey and H. E. Hoelscher, Anal. Chem., 29, 123 (1957).

The concentrations of alkyl nitrite were of the order of several hundred parts per million.

Ultraviolet spectra were determined with a Cary Model 11 Recording Spectrophotometer. Since the band system in the 3000-4000 A. region falls in both the tungsten and hydrogen lamp region, the spectra were obtained with both sources. The peak positions and intensities in the 3400-3700 A. spectral region were averaged using the values from the individual determinations with each source. The peak positions and intensities with a representative alkyl nitrite solution were checked at various mechanical slit widths and at the minimum scanning speed of 1A/second. No effect on peak maxima or intensities was observed as compared with the normal operating conditions. These conditions included mechanical slit widths of 0.04 mm. with the hydrogen lamp and 0.1 mm. with the tungsten lamp at 3700 A. The mechanical slit widths in the 2050-2250 A. region ranged from 0.1 to 2 mm., but most of the values fell around 0.2-1 mm. In this spectral region, a 1 mm. mechanical slit width corresponds to a spectral slit width of about 15 A. The spectra were scanned at 10A/second.

The wavelength maxima are reproducible to $\pm$ 5 A. and are probably accurate to within 10 A. However, the short wavelength peaks are quite broad and flat; consequently, these peaks are readable only to about $\pm$ 10 A. The molar extinction coefficients are considered to be

reproducible within two or three percent and probably are accurate to ± 5 percent. The instability of the alkyl nitrites to heat and light combined with instrumental and sample preparation errors makes it difficult to obtain highly accurate molar extinction coefficients for these nitrites.

RESULTS AND DISCUSSION

The wavelength maxima and the molar extinction coefficients obtained for the four alkyl nitrites employed in various solvent systems are listed in Tables I through IV. The peaks in the 3000-4000 A. region are designated by A through G with decreasing wavelength. The A peak is often only a shoulder on the B peak. The G peaks and sometimes the F peaks are too weak to definitely locate them. However, in many of the solutions, seven wavelength maxima are clearly identifiable in the 3000-4000 A. region. The single broad peaks which appear in the 2050-2250 A. region are designed as H peaks. Owing to the very poor transmission of most solvents in this region, wavelength maxima could be obtained only in cyclohexane, isooctane, diethyl ether, methanol, isopropanol, and water. The butyl and amyl alcohols are not sufficiently transparent in this region. Lower alcohols such as methanol and i-propyl alcohol, which can be purified sufficiently for use in the 2050-2250 A. region were used for qualitative purposes, but not for quantitative determinations because of transesterification resulting in appreciable conversion of the nitrites present to methyl and i-propyl nitrite.

The solvent effects on the wavelength maxima of the t-alkyl nitrites appear to be different from those observed for the n- and

i-alkyl nitrites. The wavelength maxima in the 3000-4000 A. range for t-butyl nitrite in cyclohexane, isooctane and carbon tetrachloride appear in essentially the same positions as in the gas phase.[8] However, in acetone and water, the wavelength maxima appear to shift downwards by 50 to 100 A. The wavelength maxima for n- and i-alkyl nitrites in nonpolar and slightly polar solvents are essentially the same as the peaks observed in the gas phase.[8,11] The peak maxima appear to shift slightly upwards in wavelength in acetone and water. Actually, the wavelength maxima for all the alkyl nitrites in acetone and water appear at about the same positions. It should be noted that previous work[11] also shows a slight upward shift in peak maxima for n and i-alkyl nitrites when passing from the nitrites in gas state to the nitrites in nonpolar solvents and then into acetonitrile and dimethyl formamide as solvents.

The p-dioxane showed pecularities as a solvent for alkyl nitrites. The wavelength maxima of the alkyl nitrites in p-dioxane closely approximated those in acetone despite wide differences in polarity.

While the spectra of the n- and i-alkyl nitrites in ethyl acetate were normal, t-butyl nitrite showed anomalous behavior. The wavelength maxima were very weak, and a definite doubling of peaks occurred as if additional band system were appearing in this one instance. Possibly this result is due to transesterification forming some ethyl nitrite.

All of the molar absorption coefficients (moles^{-1} liter cm^{-1}) were less than 100 for members of the band system in the 3000-4000 A. region in all of the solvents used. The low intensities tempt one to associate these band systems with a forbidden n --> π transition. It

has been suggested that the band maxima around 3500 A. found for the nitrite ion is the result of a similar transition in which one of the unshared electrons on the nitrogen atom is raised to an antibonding π orbital of the ion.[17] In alkyl nitrites, nitrous acid, dinitrogen

(17) W. G. Trawick and W. H. Eberhardt, J. Chem. Phys. 22, 1462 (1954).

tetroxide, dinitrogen tetroxide-solvent complexes,[18] nitrosamines, and

(18) A. P. Altshuller, J. Phys. Chem., 62 (1958).

nitrite ion, a weak band is present around 3500 A. One might consequently associate an n --> π electronic transition with all of these bands. There is some difference in these band systems in that the alkyl nitrites, nitrous acid, dinitrogen tetroxide-solvent complexes, and nitrosamines show vibrational fine structure whereas dinitrogen tetroxide and nitrite ion show only a single broad band. Unfortunately, the data presented on the ultraviolet spectra of alkyl nitrites in various solvents here and elsewhere[11,12] do not give convincing evidence for the blue shift which has been found to arise from n --> π type electronic transitions.[19]

(19) H. McConnell, J. Chem. Phys. 20, 700 (1952).

It has been pointed out previously in the literature[11] that the intensity ratio in n and i-alkyl nitrites of the two peaks on either side of the most intense maxima at about 3560 A. varies with the solvent. That is, the D peak is more intense than the B peak in nonpolar and slightly polar solvents, but the opposite is true in highly polar

solvents such as acetonitrile and dimethylformamide.[11] Similarly, in this study, the same effect is noticeable going from nonpolar to the polar solvents, acetone and water. Although the intensities of the nitrites in water were not obtained quantitatively, the B peak is more intense than the D peak.

This variation in intensity ratio may be associated with the variation in the ratio of cis to trans rotational isomer with solvent. The rotational isomerism of alkyl nitrites is well established.[20,8,10,11]

(20) Dior and P. Tarte, J. Chem. Phys., 19, 1064 (1951).

It has been shown in the gas state that the trans-form predominates (except for methyl nitrite), but that the ratio of trans to cis isomer increases in the order tertiary > secondary > primary nitrite.[7] It seems also reasonable that a change in solvent from nonpolar to highly polar might affect this ratio also.

In t-butyl nitrite, the B peak is more intense than the D peak, irrespective of solvent. If a ratio of B/D of greater than unity can be associated with a large preponderence of the trans-form for t-butyl nitrite in solution, as in the gas phase, then the n- and i-alkyl nitrites would be shifted toward a larger proportion of the trans-form with increasing dielectric constant of the solvent.

The lack of a blue shift in n- and i-alkyl nitrites for the 3000-4000 A. band system, if it actually does result from a n --> π^* type electronic transition, may be associated with the shift in isomeric ratio acting in an opposite direction to the usual solvent effect in shifting the peak maxima. If the cis to trans ratio is less sensitive

to solvent in t-alkyl nitrites, then the blue shift might be expected to show itself. Indeed, this is confirmed experimentally if the blue shift found for t-butyl nitrite in acetone and water is genuine.

Relatively few data have been available on the short wavelength peaks in alkyl nitrites. It has been reported[9,10] that n-butyl- and n-amyl nitrite in a light petroleum mixture showed maxima at 2220 and 2185 A, respectively, and that n-butyl nitrite has a maximum at 2180 A. in ethanol. The present work indicates that the alkyl nitrites show maxima in the 2210 to 2240 A. region in hydrocarbons. It was also found that the n- and i-amyl nitrites exhibit maxima at about 2220 A. in the gas state. When diethyl ether is used as a solvent, the maxima are found at about 2210 A. In isopropanol, the alkyl nitrites show absorption maxima between 2170 and 2220 A., while in methanol these compounds show peak maxima between 2110 and 2160 A. The alkyl nitrites have absorption maxima between 2080 and 2100 A. in water. The slightly higher wavelengths for the peaks in hydrocarbons compared with the gas state may indicate a red shift owing to polarization.[21] However,

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(21) N. S. Bayliss and E. G. McRae, J. Phys. Chem., 58, 1002, 1006 (1954).

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the more important characteristic of the data is the quite definite blue shift associated with the short wavelength bands.[19,21]

The absorption maxima in the 2050 to 2250 A. region have molecular absorption coefficients in the 1000 to 2000 $mole^{-1}$ liter cm^{-1} range. These intensities, along with the definite blue shift shown by this band, strongly suggest the assignment of the band as an allowed singlet-singlet $n \rightarrow \pi^*$ transition.

Acknowledgement: The authors wish to thank Donald Stephens for assistance in obtaining some of the ultraviolet spectra during the course of this investigation.

Table I. Ultraviolet Absorption Spectra of n-Amyl Nitrite in Various Solvents

Solvent	Wavelengths (A) and Molecular Extinction Coefficients ($Mole^{-1}$ Liter Cm^{-1})							
	A	B	C	D	E	F	G	H[a,b]
Cyclohexane	3830 28	3700 60	3560 74	3445 65	3335 46	3235 31	3140 25	2240 1780
Isooctane	3830 27	3690 56	3560 69	3440 60	3330 43	3230 28	3140 23	2240 1760
Carbon Tetrachloride	3825 34	3695 73	3560 87	3440 76	3330 54	3230 36	3140 27	- -
Chlorobenzene	- -	3700 78	3565 93	3445 81	3335 57	3240 37	3145 28	- -
Diethyl Ether	3840 31	3690 66	3560 80	3440 69	3330 49	3235 32	3145 24	2210 1470
Di-i-propyl Ether	3840 33	3690 69	3560 83	3440 73	3330 51	3230 33	3140 25	
p-Dioxane	3870 30	3710 59	3570 67	3450 57	3345 39	3240 27	3140 24	- -
Ethyl Acetate	3840 22	3700 46	3560 54	3445 45	3335 32	3240 22	3140 17	- -
Acetone	3880 30	3720 57	3565 66	3445 56	3340 39	- -	- -	- -

(continued)

Table I. Ultraviolet Absorption Spectra of n-Amyl Nitrite in Various Solvents

Solvent	Wavelengths (A) and Molecular Extinction Coefficients (Mole^{-1} Liter Cm^{-1})							
	A	B	C	D	E	F	G	H[a,b]
n-Amyl Alcohol	3840	3695	3560	3445	3335	3235	3145	-
	27	58	70	61	44	28	21	-
Water	3860	3710	3570	3460	-	-	-	2100

[a] H peak at 222 mμ in gas. Peaks in 3000-4000 A. region for n-amyl nitrite as gas at 3840 A., 3680 A., 3560 A., 3430 A., 3330 A., 3220 A. and 3130 A.

[b] H peak at 2140 A. in methanol and at 2220 A. in isopropanol.

Table II. Ultraviolet Absorption Spectra of i-Amyl Nitrite in Various Solvents

Solvent	Wavelengths (A) and Molecular Extinction Coefficients (Mole^{-1} Liter Cm^{-1})							
	A	B	C	D	E	F	G	H[a,b]
Cyclohexane	3840 33	3690 68	3560 83	3440 72	3330 51	3230 34	3135 29	2240 1960
Isooctane	3830 26	3690 59	3560 74	3440 64	3325 45	3230 28	3140 19	2235 1810
Carbon Tetrachloride	- -	3690 75	3550 90	3440 78	3330 57	3230 36	3140 31	- -
Chlorobenzene	- -	3690 82	3560 98	3440 85	3335 60	3235 39	3145 30	- -
Diethyl Ether	3840 32	3700 66	3560 79	3445 68	3335 48	3235 32	3145 24	2210 1610
Di-i-propyl Ether	3840 33	3695 68	3560 81	3440 70	3335 50	3235 33	3140 26	- -
p-Dioxane	3850 33	3720 64	3580 70	3450 57	3345 40	3245 25	3150 20	- -
Ethyl Acetate	3850 29	3700 56	3565 68	3445 58	3340 41	3240 27	3145 20	- -

Table II. Ultraviolet Absorption Spectra of i-Amyl Nitrite in Various Solvents

Solvent	Wavelengths (A) and Molecular Extinction Coefficients ($Mole^{-1}$ Liter Cm^{-1})							
	A	B	C	D	E	F	G	H[a,b]
Acetone	3860	3705	3570	3445	3335	3220	-	-
	33	63	72	60	42	34	-	-
i-Amyl Alcohol	3830	3695	3560	3440	3335	3230	3140	2275
	33	70	84	73	52	35	26	1460
Water	3860	3710	3575	3455	3350	-	-	2080

[a] H peak at 222 mμ in gas.

[b] H peak at 2110 A. in methanol and 2190 A. in propanol.

Table III. Ultraviolet Absorption Spectra of n-Butyl Nitrite in Various Solvents

Solvent	Wavelengths (A) and Molecular Extinction Coefficients ($Mole^{-1}$ Liter Cm^{-1})							
	A	B	C	D	E	F	G	H[a]
Cyclohexane	3840	3695	3560	3440	3330	3230	3140	2230
	32	70	85	74	53	36	29	1410
Isooctane	3840	3695	3560	3440	3330	3230	3140	2200
	30	66	82	72	52	34	24	1440
Carbon Tetrachloride	3830	3695	3560	3440	3330	3230	3140	-
	33	69	82	72	52	34	26	-
Chlorobenzene	-	3690	3560	3445	3335	3235	3145	-
	-	70	84	73	51	34	24	-
Diethyl Ether	3840	3700	3560	3445	3335	3235	3140	2210
	29	67	81	70	48	32	22	1510
Di-i-propyl Ether	3840	3690	3560	3440	3330	3230	3140	
	34	69	84	73	52	34	26	
p-Dioxane	3880	3710	3570	3450	3340	3240	-	-
	31	58	65	54	38	25	-	-
Ethyl Acetate	3850	3700	3565	3445	3335	3240	3140	-
	30	59	70	59	42	27	21	-

(continue.)

Table III. Ultraviolet Absorption Spectra of n-Butyl Nitrite in Various Solvents

Solvent	Wavelengths (A) and Molecular Extinction Coefficients ($Mole^{-1}$ Liter Cm^{-1})							
	A	B	C	D	E	F	G	H[a]
Acetone	3880	3720	3585	3460	3340	-	-	-
	28	53	59	50	38	-	-	-
n-Butyl Alcohol	3840	3695	3560	3440	3335	3235	3145	-
	28	61	74	64	46	30	24	-
Water	3860	3705	3575	3460	-	-	-	2100

[a] H peak at 2150 A. in methanol and at 2170 A. in isopropanol.

Table IV. Ultraviolet Absorption Spectra of t-Butyl Nitrite in Various Solvents

Solvent	Wavelengths (A) and Molecular Extinction Coefficients ($Mole^{-1}$ Liter Cm^{-1})							
	A	B	C	D	E	F	G	H[a]
Cyclohexane	3970	3820	3660	3530	3405	3295	-	2210
	53	82	73	48	25	15	-	1680
Isooctane	3980	3820	3660	3520	3405	3285	-	2210
	35	54	48	30	15	8	-	1710
Carbon Tetrachloride	3970	3810	3660	3520	3405	3290	-	-
	47	71	62	41	23	12	-	-
Chlorobenzene	3970	3800	3660	3520	3400	3285	-	-
	44	68	61	41	25	17	-	-
Diethyl Ether	3970	3810	3660	3530	3400	3295	-	2210
	46	72	64	41	21	9	-	1790
Di-i-propyl Ether	3980	3810	3660	3530	3400	3295	-	-
	46	71	64	40	21	11	-	-
p-Dioxane	3880	3730	3600	3480	3380	-	-	-
	33	52	51	37	24	-	-	-
Ethyl Acetate[b]	3970	3800,3730	3660,3600	3520	3395	3275	3165	-
Acetone	3880	3730	3595	3495	3400	3300	-	-
	30	49	51	40	37	27	-	-

Table IV. Ultraviolet Absorption Spectra of t-Butyl Nitrite in Various Solvents

Solvent	Wavelengths (A) and Molecular Extinction Coefficients ($Mole^{-1}$ Liter $Cr.^{-1}$)							
	A	B	C	D	E	F	G	H[a]
t-Butyl Alcohol	3970	3805	3660	3525	3405	3295	-	-
	33	52	44	29	14	7	-	-
Water	3840	3700	3575	3455	-	-	-	2100

[a] H peak at 2160 A. in methanol and at 2210 A. in isopropanol.

[b] Weak diffuse peaks.